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PTO 05-4122

Japanese Kokai Patent Application
No. Sho 63[1988]-100391

MOLDED PHOSPHOR BODY AND MOLDED PHOSPHOR BODY MANUFACTURING METHOD

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UNITED STATES PATENT AND TRADEMARK OFFICE
WASHINGTON, D.C. JUNE 2005
TRANSLATED BY THE MCELROY TRANSLATION COMPANY

JAPANESE PATENT OFFICE
PATENT JOURNAL (A)
KOKAI PATENT APPLICATION NO. SHO 63[1988]-100391

Int. Cl.[4]:	G 01 T 1/20 C 09 K 11/00
Sequence Nos. for Office Use:	B-8406-2G E-7215-4H
Filing No.:	Sho 61[1986]-143081
Filing Date:	June 20, 1986
Publication Date:	May 2, 1988
No. of Inventions:	2 (Total of 6 pages)
Examination Request:	Not filed

MOLDED PHOSPHOR BODY AND MOLDED PHOSPHOR BODY MANUFACTURING METHOD

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[Amendments have been incorporated into the text of the translation.]

Claims

1. A molded phosphor body characterized in that it is composed of a mixture of an epoxy resin and hardener that has low viscosity at normal temperature or when heated and that is obtained after hardening by precipitating a phosphor powder after a phosphor powder is dispersed into the epoxy composition solution that is light-permeable and the epoxy composition solution is heat-hardened.

2. A molded phosphor body characterized in that, in Claim 1, a low-viscosity bisphenol A type epoxy resin that has an epoxy equivalence of 170-180 is used as the aforementioned epoxy resin and a low-viscosity acid anhydride compound is used as the aforementioned hardener, and a quaternary ammonium salt composed of an alkyl group that has a carbon number of at least 8 and

that is at least one substituted group of four substituted groups is used as a hardening promoter, and an epoxy composition solution that is light-permeable is used after hardening of the mixture of the aforementioned three substances.

3. A molded phosphor body characterized in that 90-110 phr of 3 or 4 methyl hexahydrophthalic anhydride is used as the acid anhydride compound described in Claim 2, and 0.1-1.0 wt% of tetradecyl dimethyl benzyl ammonium chloride is used as the quaternary ammonium salt, for the mixture of epoxy resin and hardener.

4. A molded phosphor body characterized in that Gd_2O_2S: Pr, Ce, and F are used as the phosphor described in Claim 1, 2 or 3.

5. A molded phosphor body manufacturing method characterized by having a process in which a phosphor powder is dispersed into an epoxy composition solution that has low viscosity at normal temperature or with heating, a process in which the phosphor powder is precipitated, and a process in which the epoxy composition solution is heat-hardened.

Detailed explanation of the invention

Industrial field of application

The present invention pertains to the scintillator of a scintillation-type X-ray detector. In particular, it relates to a molded phosphor body that is ideal as a scintillator for a CT (Computer Tomography) X-ray detector, and to a molded phosphor body manufacturing method. /2*

Prior art

As a first example of the prior art for a powder molded phosphor body and molded body manufacturing method, a method in which a block-molded body is obtained by press-molding a phosphor powder with a hot press or hot isostatic press at high temperature and high pressure as shown in Japanese Kokai Patent Publication No. Sho 58[1983]-24088. A second example is one in which a powder and a polymer emulsion are mixed, and after drying, the powder can be molded by heating or pressing, or both, the powder to which the polymer is adhered, as shown in Japanese Kokai Patent Publication No. Sho 57[1982]-7861. A simple molding method for phosphor powder that uses a polystyrene resin emulsion is discussed as an ideal example of this method. A third example is one in which a phosphor is mixed into a liquid base substance (for example, epoxy resin) that can be hardened and that has light-permeability after hardening, a suspension is produced, the suspension is introduced into a mold with a specific shape, and the phosphor is solidified without change and is kept in a constant suspension form by hardening the base material solution, as shown in Japanese Kokai Patent Application No. Sho 54[1979]-90089.

* [Numbers in the right margin indicate pagination of the original foreign language text.]

Problems to be solved by the invention

With the aforementioned first example of the prior art, high temperature and high pressure of 1000-2000°C and 10-1000 kg/cm^3 are required, and enormous equipment is required, and the molded phosphor body portions near the container walls demonstrate degraded performance because of the dispersion of impurities from the walls of the container used. It is difficult to obtain molded phosphor bodies at low cost.

With the second prior art example, washing with an organic solvent is not possible because polystyrene has poor chemical resistance, the grinding oil used for machining penetrates voids because many voids remain in the molded body, and light-permeability is degraded, among other problems. With the third prior art example, the phosphor is solidified, remaining in a suspended state, so density cannot be increased and X-ray usage efficiency is not very good.

The objective of the present invention is to provide a molded phosphor body and molded phosphor body manufacturing method that is simple and inexpensive, has little color-degradation with X-ray exposure, can detect X rays with high sensitivity, and that has outstanding homogeneity, chemical resistance and machinability.

Means to solve the problems

The aforementioned objective is achieved by discovering a low-viscosity epoxy composition solution that is light-permeable after hardening and has little color degradation with X-ray exposure, precipitating a phosphor powder after dispersing a phosphor powder into the low-viscosity epoxy composition solution uniformly so as to include no air bubbles, and heat-hardening the epoxy composition solution.

Function

The heat-hardened epoxy composition has outstanding chemical resistance and machinability. By precipitating the phosphor powder, the density of the molded phosphor body is also greater than that of the prior art with which the phosphor powder is hardened while remaining dispersed.

Application example

Below, an application example of the present invention will be explained with figures. When a phosphor powder used to measure X-ray intensity as a scintillator, a molded body in which the phosphor powder is hardened by some method is required. In order to improve X-ray detection efficiency, it is desirable that the phosphor powder be hardened at high density and that no air bubbles be mixed in so as to eliminate loss caused by optical scattering. The auxiliary materials used for bonding the phosphor powder granules together must also not produce color degradation

by X-ray exposure during use when hardened. As a molding method for a phosphor powder that satisfies such conditions, a method will be explained that: uses a liquid substance hardened with heat and that does not discolor due to X-ray exposure after hardening as the auxiliary material used for hardening, precipitates the phosphor powder by leaving the mixed solution still after dispersing the phosphor powder uniformly in the liquid substance so as not to include air bubbles, hardens the liquid substance with heat, and that obtains a molded phosphor body from the precipitated portion.

Figure 1 shows the method for uniformly dispersing a phosphor powder into a liquid substance so as not to include air bubbles. An epoxy composition solution composed of epoxy resin, hardener, hardening promoter, etc., is used as liquid substance (16) used for binding the phosphor powder granules together. Phosphor powder (15) is mixed into this in container (14), /3 the mixed solution is agitated by agitator drive system (11) and agitator (12) in vacuum constant-temperature tank (13) that is kept at a constant temperature so that the phosphor powder is uniformly dispersed without including air bubbles. Figure 2 shows after the mixed solution is left with the mixed solution in which the phosphor powder was uniformly dispersed as described above kept at a constant temperature. The inside of container (14) that contains the aforementioned mixed solution is divided into top part (21) that is primarily an epoxy composition solution that contains hardly any phosphor powder and portion (22) in which the phosphor powder particles are precipitated. With precipitated portion (22), an epoxy composition solution is present between the phosphor powder particles in a form that binds the particles together. After the epoxy composition solution in container (14) is heat-hardened with the necessary conditions, a molded phosphor body with the required shape can be obtained by machining from precipitated portion (22).

The ratio H/D of liquid height D given by the entire mixture of phosphor powder to epoxy composition solution and height H of the portion in which phosphor powder particles are precipitated (ratio of precipitated portion height to entire density) in Figure 2 is determined by the density of the epoxy composition solution and the density of the phosphor powder mixed in. Figure 3 shows the relationship between ratio H/D of the phosphor powder precipitated portion height to overall liquid height found experimentally using a phosphor powder with a density of about 7.2 g/cm^3 and an epoxy composition solution with a density of 1.0-1.2 g/cm^3. A phosphor powder concentration of 50-70 wt% is suitable for uniformly dispersing the phosphor powder in the resin composition solution and making it easy to for air bubbles to escape from the mixed solution. When the overall liquid height is around 120 mm, the height of the phosphor powder precipitated portion will be around 30-60 mm, and a large molded phosphor body can be obtained.

In order to realize X-ray detection with high sensitivity and stable over a long period, the epoxy resin that is present in a form for binding the phosphor powder particles together must not produce extensive color degradation with long-term X-ray exposure. The following have been

proven to be suitable as epoxy composition solutions with little color degradation with X-ray exposure.

Epoxy resin: D.E.R. 332 (100 parts, bisphenol A type epoxy resin, epoxy equivalent 172-176, The Dow Chemical Company).

Acid anhydride as hardener: HN-5500E (3- or 4-methyl hexahydrophthalic anhydride, 90-110 parts, Hitachi Chemical Co., Ltd.).

Hardening accelerator: M_2-100 (tetradecyl dimethyl benzyl ammonium chloride, 0.1-1.0 wt% to abovementioned mixture of epoxy resin and hardener, NOF Corporation).

M_2-100 is a quaternary ammonium salt composed of an alkyl group that has a carbon number of at least 8 and is at least one substituted group of four substituted groups, and has sufficient solubility in an epoxy resin, a liquid anhydrous compound or a mixture. When the mixing ratio of M_2-100 is less than 0.1 wt%, a long time is required for hardening, which is not practical. When it is more than 1 wt%, discoloration after hardening is severe, which is undesirable.

The epoxy composition solution is colorless and transparent. When a phosphor powder with a density of about 7.2 g/cm^3 (particle diameter 40-50 μm) is mixed and dispersed into the solution and the temperature of the mixed solution is kept at 60-70°C, a state in which phosphor powder particles are precipitated as shown in Figure 2 is reached in about 1 h.

The use of a phosphor that has high conversion efficiency from X ray to light is desirable for a scintillator for an X-ray detector. Particularly for a phosphor suited for a CT X-ray detector, the Gd_2O_2S: Pr, Ce, F, which is one such reported in Japanese Kokoku Patent No. Sho 60[1985]-4856, is an optimal one. A phosphor powder with particle diameter 40-50 μm (about 7.2 g/cm^3 density), Gd_2O_2S: Pr, Ce, F was mixed and dispersed into the aforementioned resin composition solution and precipitated, and a molded phosphor body was obtained by gelling for 22 h at 80°C and curing for 14 h at 100°C. The density of the molded phosphor body was about 4.2 g/cm^3 and homogenous. Experimental results for sensitivity degradation caused by X-ray (120 kVp) exposure of the molded phosphor body over a long time are shown in Figure 4A.

Figure 4B shows sensitivity degradation caused by X-ray (120 kVp) exposure of a phosphor (Gd_2O_2S: Pr, Ce, F) based on a manufacturing method for a molded phosphor body using the present invention that uses a commercially available transparent, low-viscosity epoxy resin (EPO-TEK 301-2, Epoxy Technology Inc.). The difference in sensitivity degradation between /4
A and B in Figure 4 is due to the epoxy composition solution. The vertical axis in Figure 4 is normalized for sensitivity when there is no X-ray exposure. With Application Example A based on the present invention, there are absolutely no problems in actual use when sensitivity degradation of only about 10% is demonstrated due to X-ray exposure of several 10,000 roentgens.

The table below is a relative comparison of sensitivity to X rays at 120 kV of a molded phosphor body based on the present invention with both sensitivity of a molded phosphor body using a polystyrene resin emulsion based on a conventional invention (Chuken 23, 804) and sensitivity of a monocrystalline scintillator under conditions assuming a CT X-ray detector.

シンチレータ	厚さ(mm)	相対感度
本発明による蛍光体成型体	1.0	1.3
従来発明による蛍光体成型体	1.0	1.0とする
$CdWO_4$(単結晶)	3.0	1.0～1.1

Key:
1 Scintillator
2 Thickness
3 Relative sensitivity
4 Molded phosphor body based on the present invention
5 Molded phosphor body based on conventional invention
6 Considered to be 1
7 $CdWO_4$ (monocrystal)

The X-ray sensitivity of the molded phosphor body based on the present invention in this way is greater than that of a $CdWO_4$, which is a monocrystal, and has sensitivity improved more 30% or more over a molded phosphor body based on the prior art. In addition, the properties of outstanding chemical resistance and machinability of the epoxy-hardened substance can be effectively utilized, and a homogenous molded phosphor body that has outstanding properties can be provided at low cost with a simple method.

Above, a method using an epoxy composition solution as the medium for binding phosphor powder particles together was explained, but of course it can also be applied in place of an epoxy resin composition to a liquid substance that is transparent after hardening and that will produce no color degradation with X-ray exposure.

An ideal application for the molded phosphor body obtained with the present invention is as a scintillator for an X-ray CT detector. Figure 5 shows an example in which a molded phosphor body obtained with the present invention is applied to an X-ray detector for what is called third-generation X-ray CT. An X-ray beam (52) from X-ray tube (51) passes through analyzed body (53), reaches scintillator (54) made with a molded phosphor body based on the present invention, and light emission from the scintillator is detected by light-receiving element (55).

Effect of the invention

With the present invention, after a phosphor powder is uniformly dispersed into an epoxy composition solution and precipitated, the epoxy resin composition is heat-hardened and a molded phosphor body can be obtained. So, it is possible to provide a low-cost molded phosphor body with outstanding chemical resistance and machinability, which are features of epoxy-hardened substances, and that also has outstanding homogeneity with a simple method.

Brief description of the figures

Figure 1 is a cross section showing a method for uniformly dispersing a phosphor powder into a liquid substance to include no air bubbles. Figure 2 is a cross section showing the obtained phosphor powder particles precipitated after the phosphor powder is uniformly dispersed into an epoxy composition solution and left still. Figure 3 shows the ratio of the height of the precipitated phosphor powder portion to the overall liquid height of the mixture of phosphor powder and epoxy composition solution. Figure 4 shows sensitivity degradation of several molded phosphor bodies due to X-ray exposure. Figure 5 is a plan view showing application of this invented molded phosphor body to an X-ray CT detector.

(14) … container, (12) … agitator, (15) … phosphor powder, (16) … epoxy composition solution, 22) … precipitated phosphor powder portion, (54) … scintillator, (55) … light-receiving element.

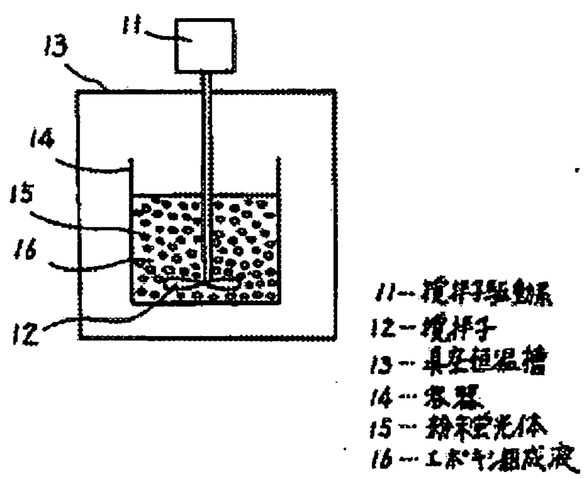

Figure 1

Legend:	11	Agitator drive system
	12	Agitator
	13	Vacuum constant-temperature tank
	14	Container
	15	Phosphor powder

16 Epoxy composition solution

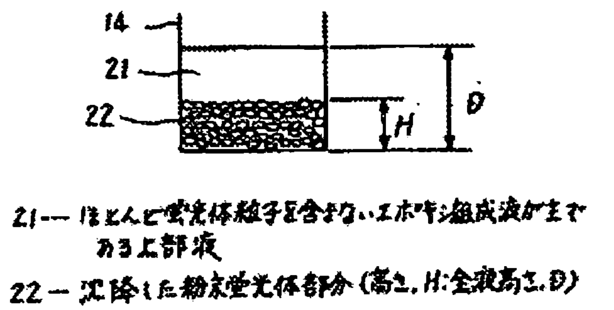

Figure 2

Legend: 21 Top liquid that is primarily epoxy composition solution containing hardly any phosphor particles

22 Precipitated phosphor powder portion (height: H, overall liquid height: D)

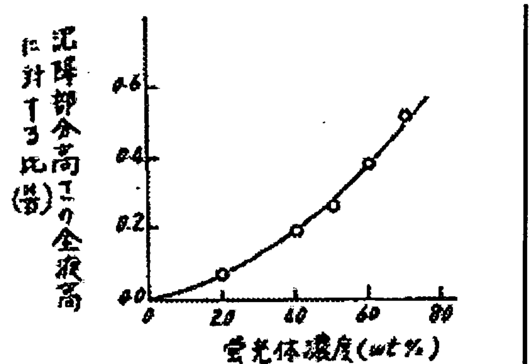

Figure 3

Key: 1 Ratio of height of precipitated portion to overall liquid height (H/D)

2 Phosphor concentration (wt%)

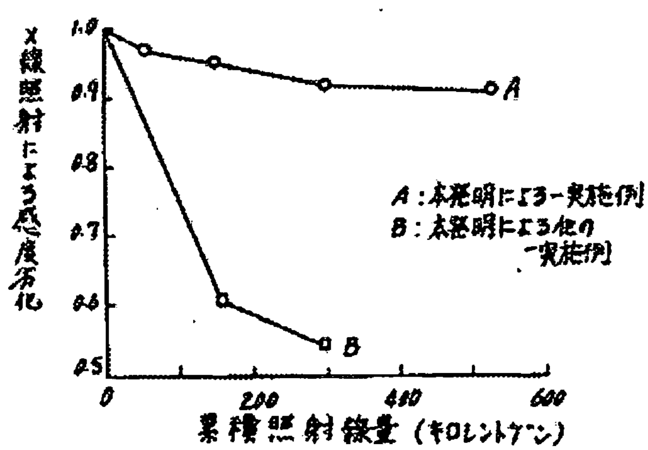

Figure 4

Key: A One application example based on the present invention
B Another application example based on the present invention
1 Sensitivity degradation due to X-ray exposure
2 Amount of cumulative exposure (kiloroentgen)

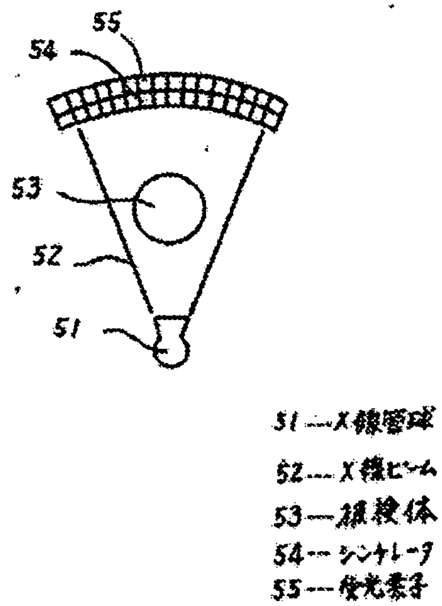

Figure 5

Legend:
51 X-ray tube
52 X-ray beam
53 Analyzed body
54 Scintillator
55 Light-receiving element